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Application of Aluminum, Copper and Gold Electrodes in AC Polymer
Light-Emitting Devices

by

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Epstein

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13. ABSTRACT (Maximum 200 words)

Symmetrically configured AC light-emitting (SCALE) '5-layer' devices having the configuration M/EB/P/EB/ITO, where M=Al, Cu or Au, EB=polyaniline (emeraldine base), P=poly (2,5 dihexadecanooxy phenylene vinylene pyridyl vinylene) or PPV-PPyV, and ITO=indium-tin oxide glass, show electroluminescent properties in both forward and reverse bias modes. In the absence of emeraldine base, in the case of aluminum and copper, electroluminescence is observed only in the forward bias mode; in the case of gold no electroluminescence is observed in either forward or reverse bias modes. The electrical properties of the '5-layer' devices (M=Al, Cu) are most surprising since their total resistance at a given applied voltage is significantly less than that of the corresponding devices in which the two polyaniline insulator layers are not present.

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Application of aluminum, copper and gold electrodes in a.c. polymer light-emitting devices

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Abstract

Symmetrically configured a.c. light-emitting (SCALE) '5-layer' devices having the configuration M/EB/P/EB/ITO, where M = Al, Cu or Au, EB = polyaniline (emeraldine base), P = poly(2,5-dihexadecanoxo phenylene vinylene pyridyl vinylene) or PPV-PPyV, and ITO = indium-tin oxide glass, show electroluminescent properties in both forward and reverse bias modes. In the absence of emeraldine base, in the case of aluminum and copper, electroluminescence is observed only in the forward bias mode; in the case of gold no electroluminescence is observed in either forward or reverse bias modes. The electrical properties of the '5-layer' devices (M = Al, Cu) are most surprising since their total resistance at a given applied voltage is significantly less than that of the corresponding devices in which the two polyaniline insulator layers are not present.

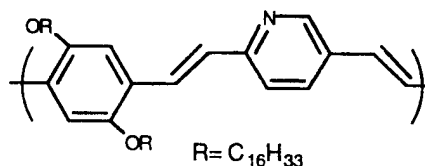
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1. Introduction

Conjugated polymers have been studied extensively for their electrical conductivity, interesting optical and, more recently, electroluminescence (EL) properties [1–7]. Conjugated polymer light-emitting diodes (CPLEDs) were first reported in 1990 using poly(phenylene vinylene) (PPV), as the light-emitting material [1]. PPV thus became the model compound for the study of CPLED properties. Even today PPV and its derivatives remain the most popular polymers for fabricating CPLED devices.

The EL properties of polypyridine [5] and poly(pyridylvinylene) [7,8], a copolymer of a derivative of PPV and the nitrogen analog of PPV, poly(2,5-dihexadecanoxo phenylene vinylene pyridyl vinylene) (PPV-PPyV) [9] (as shown in Scheme 1), have been reported previously.

The polymer backbone of the copolymer is isoelectronic with that of PPV and its derivatives. The nitrogen can also be protonated and alkylated [8,10,11], raising the possibility for fine-tuning of its photoluminescence (PL) [11] and EL [8] spectra. This compound presents a distinct advantage as compared to PPV in fabricating CPLED devices, since it is soluble in a variety of organic solvents including CHCl₃, xylene, THF, etc., and is somewhat soluble in 98% HCOOH. In the past, CPLED devices have usually been operated in the forward bias mode only, the indium-tin oxide (ITO)



Scheme 1. Molecular structure of PPV-PPyV.

glass being attached to the positive terminal of the d.c. power supply. More recently a few reports have appeared involving operation of these devices in the reverse bias mode [12–15] although such operation, at least in certain cases [12,13], results in rapid breakdown of the device. Both symmetric and asymmetric current-voltage (*I*-*V*) curves have been reported, but even in the almost symmetrical *I*-*V* curve case the EL intensity while operating in an a.c. mode may differ in the forward and reverse bias modes [14].

We report here a continuation [16–18] of our studies on the use of Au as both an electron and as a hole injection electrode, in particular, comparing the use of Al, Cu or Au as the metal electrodes in symmetrically configured a.c. light-emitting (SCALE) devices [16]. All can be operated in forward and reverse bias modes and in an a.c. mode. Thus, both the metal and ITO electrodes are capable of injecting electrons and holes into the electroemissive polymer.

2. Experimental

The synthesis and characterization of the PPV-PPyV [10] copolymer have been reported earlier. All polymer solutions were filtered through a 0.2 μm Spartan filter and were spin-cast from about a 1 wt.% PPV-PPyV solution in CHCl_3 . An ITO glass substrate with a sheet resistance of about 100 Ω/\square (Delta Technology Inc.) was cleaned by ultrasonication in a mixture of isopropanol and water (1:1) [19]. Al, Cu and Au were vacuum-deposited on top of the polymer under 2×10^{-6} Torr, the rate of deposition being 1–2 $\text{\AA}/\text{s}$ to give an emitting area of 4 mm^2 . A typical CPLED device had an active polymer layer thickness of about 1500 \AA and Al and Cu layers of about 2000 and 1000 \AA of Au, respectively.

Thickness measurements were carried out with a Tencor Co. profilometer. PL spectra were obtained with a PTI fluorescence spectrometer in air. The excitation wavelengths used were the absorption maxima in the UV-Vis spectra. EL spectra were measured using the PTI spectrometer and a Lambda LPD-421A-FM d.c. power supply. An a.c. sinusoidal voltage was generated by a Tektronix CFG 250 function generator connected to a Hewlett Packard 6827A bipolar power supply/amplifier. UV-Vis spectra of polymer films were obtained using a Perkin-Elmer Lambda 9 UV-Vis-NIR spectrometer. The turn-on potential for the CPLED devices described below was taken as the potential at which a non-zero current was visually clearly apparent from a linear plot of the I - V curves. All fabrication of devices and all measurements were performed in air.

3. Results

3.1. Al/PPV-PPyV/ITO/glass device [9,20]

The forward bias current is obtained when the ITO electrode is positively biased and the Al electrode is negatively biased. The device was fabricated by spin-casting PPV-PPyV from CHCl_3 solution on an ITO glass electrode. An Al layer (about 2000 \AA) was later vacuum-deposited. The turn-on voltage was about 13.5 V. The device did not operate in a reverse bias mode up to about 25 V at which value no significant current was observed. Visible light is observed in the forward bias mode in a dimly lit room at a current density of about 0.3 mA/mm^2 .

3.2. Cu/PPV-PPyV/ITO/glass device

The I - V characteristics are given in Fig. 1. Current was observed in both the forward and reverse bias modes. The turn-on voltage is about 22 V in the forward bias and about 15 V in the reverse bias mode. Light emission was observed in the forward bias mode only. The EL spectrum of this device is shown in Fig. 2. Visible light is observed in the forward bias mode in a dimly lit room at a current density of about 0.025 mA/mm^2 .

3.3. Au/PPV-PPyV/ITO/glass device

Ohmic behavior was observed in this device between -20 V (about 9 mA/mm^2) and about 20 V (about 11 mA/mm^2) and no light emission was observed in either forward or reverse bias mode. Similar results were obtained using approximately 700 or 1500 \AA evaporated Au films. This absence of light emission is possibly due to the extensive diffusion of Au into the emissive polymer.

3.4. Al/EB/PPV-PPyV/EB/ITO/glass SCALE device [9,20]

This device was constructed by spin-casting the polyaniline, emeraldine base (EB) from 1 wt.% EB solution in NMP on top of the ITO glass. After depositing the PPV-PPyV layer from CHCl_3 solution on top of the EB, another layer of EB was spin-cast from 1 wt.% EB solution in NMP on top of the PPV-PPyV layer, upon which the Al layer was then deposited. The I - V characteristics are given in Fig. 3(a). This device is operated in both forward and reverse bias modes at approximately the same turn-on potentials (about ± 5.0 V). It is also operated in an a.c. mode at 1 Hz (Fig. 4) to 60 Hz.

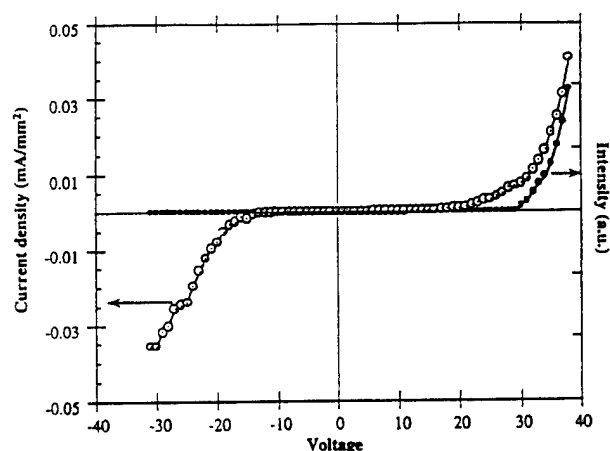


Fig. 1. I - V characteristics of a Cu/PPV-PPyV/ITO device: ●, intensity of emitted light; ○, current density.

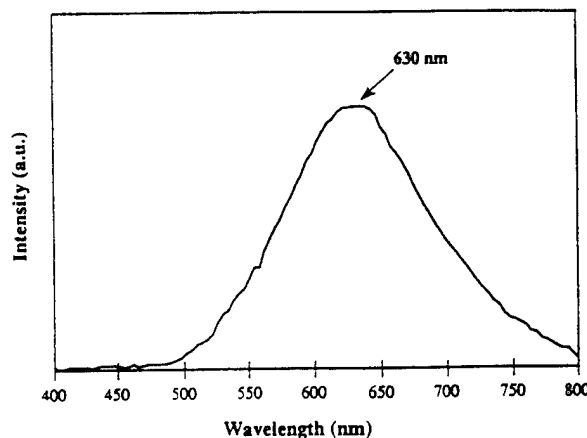


Fig. 2. EL spectrum of a Cu/PPV-PPyV/ITO device in forward bias mode at 35 V.

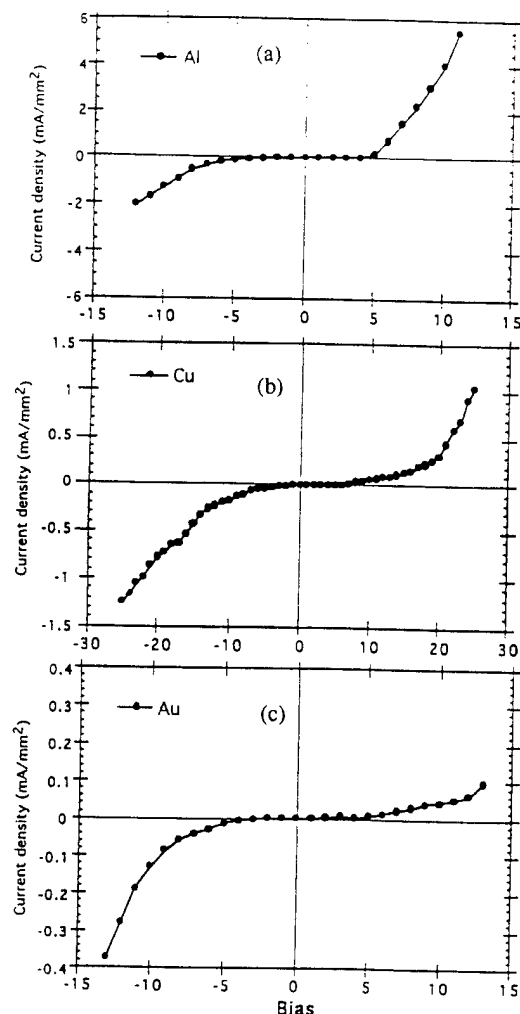


Fig. 3. I - V characteristics of SCALE devices using (a) Al, (b) Cu and (c) Au, as the metal electrode.

It should be noted that the intensity of the emitted light and the current density are more intense in the forward bias mode than in the reverse bias mode at the same applied potentials (± 8 V). Visible light is observed in the forward bias mode in a dimly lit room at a current density of about 0.18 mA/mm^2 .

3.5. Cu/EB/PPV-PPyV/EB/ITO/glass SCALE device [9]

This device was constructed in an similar manner to Section 3.4, except that Cu was used instead of Al. The I - V characteristics are given in Fig. 3(b). This device operates in both forward and reverse bias modes at turn-on potentials of about ± 8 V. It is also operated in an a.c. mode at 1 Hz (Fig. 4) to 60 Hz. It should be noted that the intensity of the emitted light is approximately the same in both forward and reverse bias modes at the same applied potentials (about ± 27 V). The EL spectra in forward and reverse bias modes are essentially identical ($\lambda_{\text{max}} \sim 635 \text{ nm}$) as shown in Fig. 5. Visible light in forward and reverse bias modes is observed in a dimly lit room at a current density of about 0.1 mA/mm^2 .

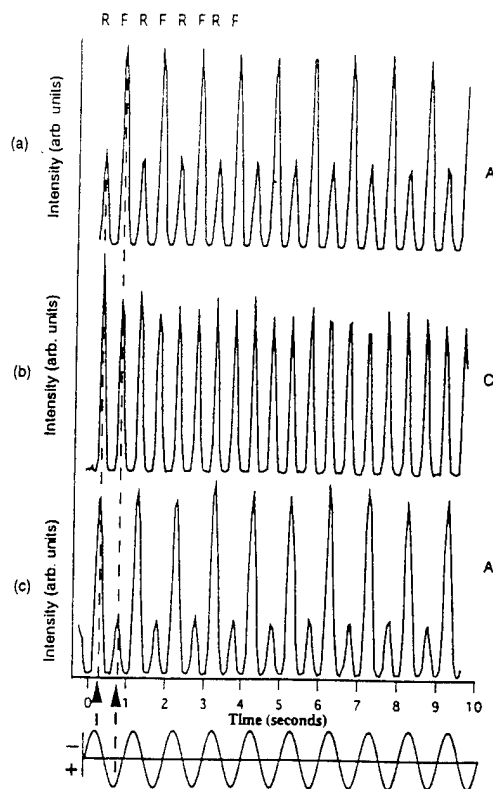


Fig. 4. EL intensity as a function of time for a metal/EB/PPV-PPyV/EB/ITO device driven by a 1 Hz sinusoidal voltage for metal: (a) Al between ± 8 V; (b) Cu between ± 27 V; (c) Au between ± 8 V.

3.6. Au/EB/PPV-PPyV/EB/ITO/glass SCALE device [18]

This device was constructed in an similar manner to Section 3.4, except that Au was used instead of Al. The device operates in both forward and reverse bias modes at turn-on potentials of about ± 5 V as shown in Fig. 3. It is also operated in an a.c. mode at 1 Hz (Fig. 4) to 60 Hz. It should be noted that the intensity of the emitted light and the current density are more intense in the reverse bias mode at the same applied potentials (about ± 8 V). Fig. 6 shows that the intensity of the emitted light is approximately proportional to the current density in both forward and reverse bias modes. The EL spectra in forward and reverse bias modes at about ± 8 V are given in Fig. 7. Visible light is observed in a dimly lit room at a current density of about 0.2 mA/mm^2 in both the reverse and forward (not shown in Fig. 6) modes.

4. Discussion

The results of this present study and of our previous studies [9,16–18,20] on polymer LED devices strongly suggest that the energy required for the injection of electrons or holes may be greatly dependent on the nature of the electrode/polymer and/or polymer/polymer interfaces. Indeed, recent very important studies have shown that vacuum deposition of metals such as Al, Na or Ca on PPV and/or related species results in the formation of chemical bonds between the metal and

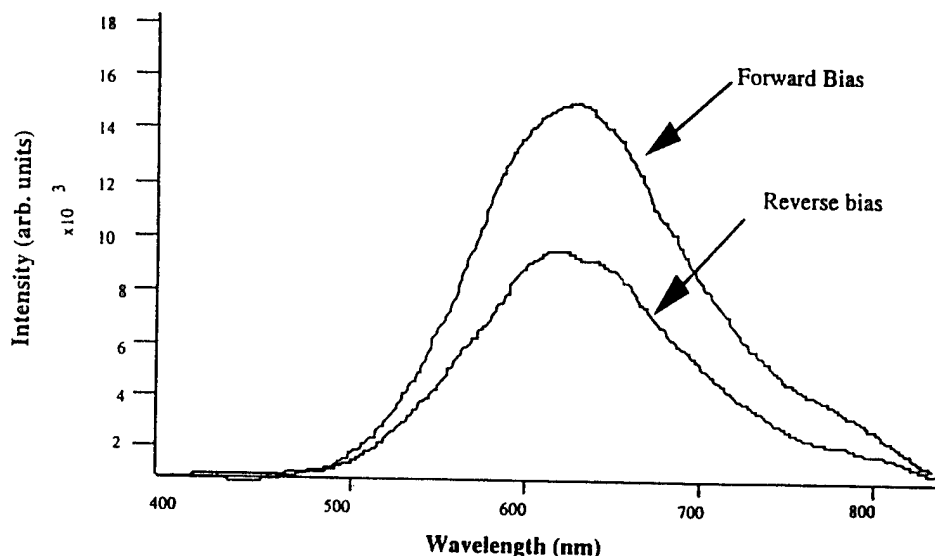


Fig. 5. EL spectra of a Cu/EB/PPV-PPyV/EB/ITO device in forward (20 V) and reverse (21 V) bias modes.

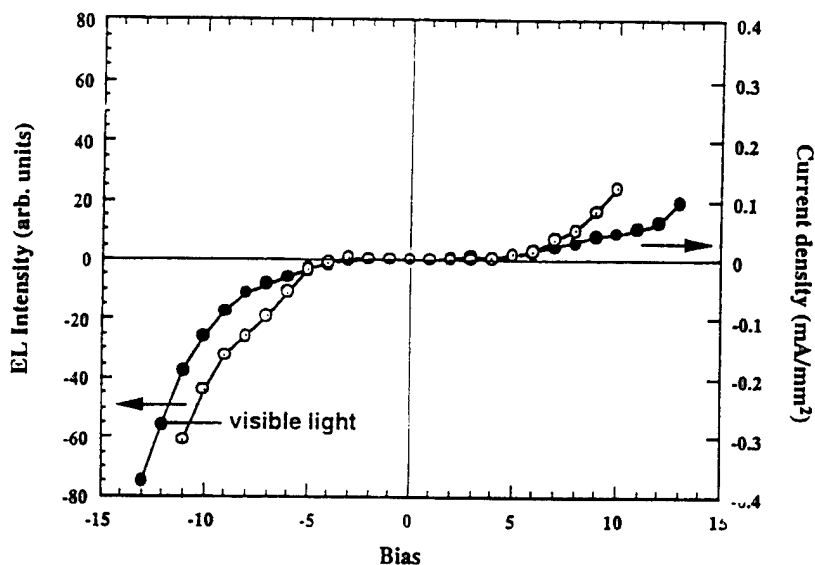


Fig. 5. Current density and intensity of light emission vs. voltage in a SCALE device using Au as a metal electrode: ○, intensity of emitted light; ●, current density.

conjugated polymer at the metal/polymer interface [21]. Little attention has been paid in previous studies of LED devices, using a conjugated electronic polymer emissive layer, to the nature of the polymer/polymer and polymer/metal interfaces (junctions) and whether such junctions show ohmic or non-ohmic behavior. Thus, for example, if an interior interface (junction) exhibits non-ohmic behavior in the potential range over which the device's EL properties are being examined, analysis of the results will undoubtedly be more complex. In addition, little attention has been paid as to whether a given electronic polymer is p-doped, n-doped or non-doped. Such properties will also greatly affect the electrical and/or the electronic properties of electrode/polymer and polymer/polymer junctions. It cannot necessarily be assumed that a given polymer is 'non-doped' just because no specific effort has been made to dope it. For example, we have previously shown that 'as synthesized' pristine 'non-

doped' *trans*-(CH)_x is actually slightly p-doped; it forms Schottky junctions with relatively low electronegative metals (Na, Ba, In) and it forms ohmic contacts with highly electronegative metals (Cu, Au, Pt) [22]. We have also shown that pristine p-type (CH)_x and p-doped poly(*N*-methylpyrrole) form a well-defined and well-characterized heterojunction, displaying highly asymmetric *I*-*V* curves [23]. The possibility of similar types of junction behavior in other LED systems must therefore be considered. Slight differences in the synthesis and handling of the polymers may drastically affect their doping and, hence, their Fermi levels and associated characteristics of the devices.

We have also shown previously [20] that certain multi-layer devices exhibit most unusual electrical properties, namely, as the number of insulating layers increases, the total resistance of the device decreases. This phenomenon is also clearly apparent in the present study. For example, the total

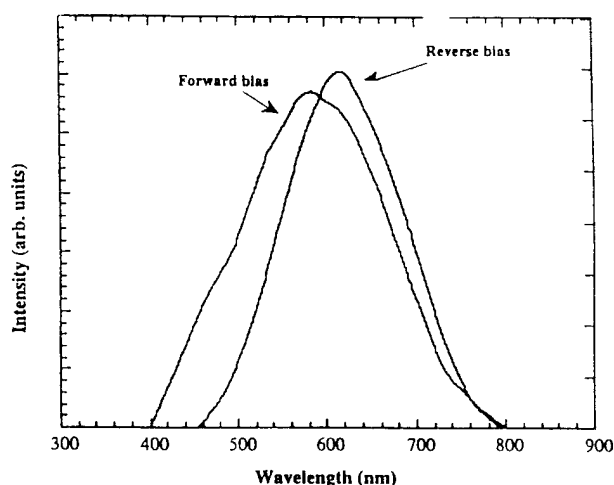


Fig. 7. EL spectra of a Au/EB/PPV-PPyV/EB/ITO device in forward and reverse bias modes at about ± 8 V. For clarity, the intensity in the forward bias mode ($\lambda_{\text{max}} = 585$ nm) has been normalized to approximately the same intensity as in the reverse bias mode ($\lambda_{\text{max}} = 616$ nm).

resistance R ($R = V/I$, where I is the current at a given applied potential, V) is about 200 times smaller at 25 V (forward bias) in a '5-layer' Cu device than in a '3-layer' Cu device even though the '5-layer' device involves two additional insulating polyaniline layers! A similar effect is noted in the reverse bias mode. Exactly the same phenomenon is observed in the '3-layer' and '5-layer' devices involving Al, the 5-layer device exhibiting a much lower total resistance than the '3-layer' device at a comparable applied potential [20]. It is noteworthy that qualitatively identical behavior has been recently observed in a separate laboratory [17b] using '3-layer' and '5-layer' Al devices using poly(*p*-pyridine), ($-\text{C}_5\text{NH}_3-$), as the emissive polymer. Unless the electrical properties of light-emitting devices are first understood it seems most unlikely that their EL properties, which are dependent on the electrical properties, can be completely understood.

It is noted that in some cases when the emissive polymer is in direct contact with the ITO, there is a significant current at high reverse voltage without detectable light emission. This is seen, for example, with Cu/PPV-PPyV/ITO and Al/EB/PPy/ITO [17b]. This suggests that electron injection from ITO to the emissive polymer is the main limiting step in light emission under reverse bias if the current is carried principally by holes, or that hole injection from the metal to the N-containing polymer is the main limiting step if the current is carried principally by electrons.

Recent studies using Au as the electron or hole injection electrode [24] in an ITO/MEH-PPV/Au (MEH = poly-(2-methoxy-5-(2'-ethyl-hexoxy)-1,4-phenylene vinylene)) device resulted in a low external quantum efficiency of 5×10^{-7} photons/electron when it was used as the electron injection electrode, but a significantly higher quantum efficiency of 4×10^{-5} photons/electron when it was used as the hole injection electrode. These values may be compared with

the value of 4×10^{-3} photons/electron when calcium was used as the electron injection electrode [24]. These phenomena have been explained by differences in the work functions of Ca (2.9 eV), Al (4.3 eV), ITO (4.7 eV) and Au (5.2 eV). Very recently a transparent Au electrode has been used as the hole injection electrode, resulting in a microcavity effect in an Al,Ca/MEH-PPV/Au LED [25]. As described below, our studies find that, when Au is used as electron and hole injection electrodes in a '5-layer' PPV-PPyV SCALE device, the intensity of the emitted light is more intense when Au is acting as a hole injection electrode (Fig. 6) as compared to when it is acting as an electron injection electrode, though the efficiency, that is, the photons/electron ratio, is nearly the same in forward and reverse biases.

4.1. Principal experimental differences between 3-layer and 5-layer (SCALE) devices employing a given metal electrode

The experimental results show that, in the M/PPV-PPyV/ITO devices ($M = \text{Al, Cu, Au}$), when $M = \text{Al}$ the device exhibits current only in the forward bias mode (about ± 20 V), whereas when $M = \text{Cu}$ the device exhibits current in both forward and reverse bias modes (about ± 30 V). Light emission is observed in the forward bias mode when $M = \text{Al}$ and Cu. No light is observed in the reverse bias mode when $M = \text{Al}$ [9,20] (no reverse bias current) or when $M = \text{Cu}$ (see Fig. 1). Ohmic behavior (no light emission) is observed when $M = \text{Au}$. It is most important to note that the incorporation of insulating films of emeraldine base (EB) on either side of the emissive PPV-PPyV layer impart dramatically different properties to the devices (see Figs. 1 and 3)! Thus, in the M/EB/PPV-PPyV/EB/ITO SCALE devices, current is observed in both forward and reverse bias modes as shown in Fig. 3; light is also observed in both forward and reverse bias modes! Furthermore, as shown in Fig. 4 the devices can operate with an a.c. applied potential: two light pulses are observed in each cycle. In addition, it is most interesting to note that, as shown in Fig. 4, at appropriately selected potentials, light emission in the forward bias mode is more intense when $M = \text{Al}$, but is more intense in the reverse bias mode when $M = \text{Au}$. When $M = \text{Cu}$, the intensities in the forward and reverse bias modes are approximately the same at about ± 27 V, although at ± 20 V (see Fig. 9) the forward bias current is greater than the reverse bias current.

As seen from Fig. 8, in the case of Au, the intensity of the emitted light in the reverse bias mode is always greater than that for the forward bias mode over the voltage range studied and the relative intensities of the reverse and forward bias modes do not change significantly with applied voltage. However, when $M = \text{Cu}$, the relative intensities do change significantly with applied voltage as shown in Fig. 9. As seen from Fig. 3, the turn-on potential when $M = \text{Cu}$ is about ± 8 V, whereas in devices with $M = \text{Al}$ and Au the turn-on potentials

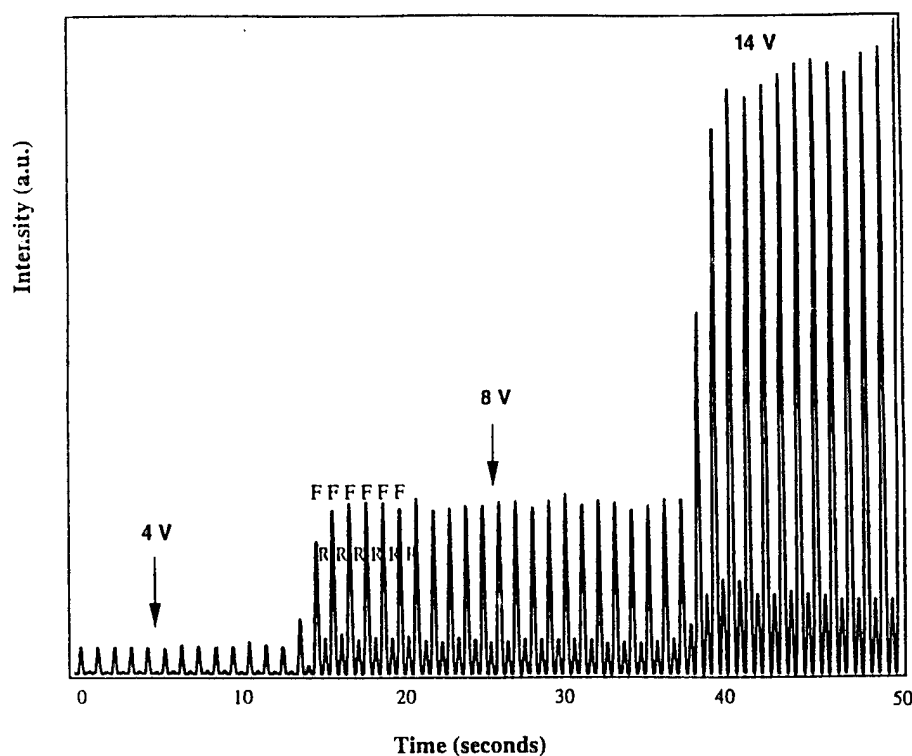


Fig. 8. Relative intensities of EL in a Au/EB/PPV-PPyV/EB/ITO device as the applied potential is increased from ± 4 , ± 8 , to ± 14 V.

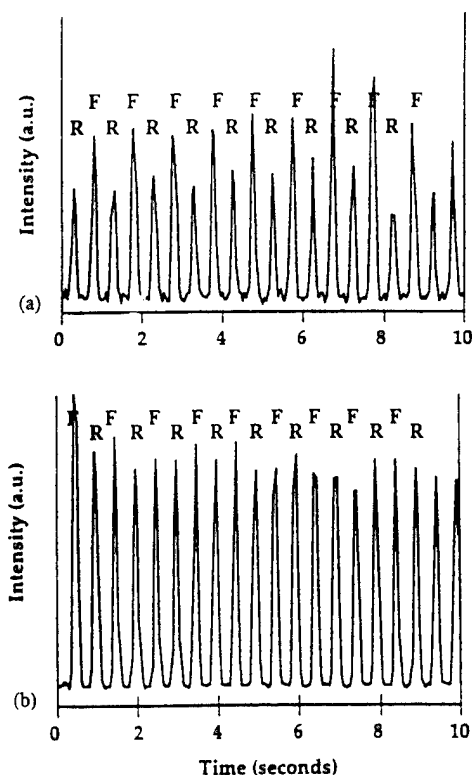


Fig. 9. Relative intensities of EL in a Cu/EB/PPV-PPyV/EB/ITO device when the applied potential is (a) 20 V and (b) 27 V.

are both at about ± 5 V. These data together with the shape of the I - V curves (Fig. 3) show that the need for a higher voltage for $M = \text{Cu}$ in Fig. 4 is to be expected, since essentially no significant current flows at 8–10 V, the voltages used for $M = \text{Al}$ and $M = \text{Cu}$ in Fig. 4.

From Fig. 6 it is noted that, for either polarity, the intensity of the emitted light is approximately proportional to the current when $M = \text{Au}$ with slightly higher efficiencies, but lower current in the forward direction. The EL spectra in the forward and reverse bias modes (Fig. 7) in this device differ somewhat, possibly because of site selective EL under weak emission conditions somewhat altering the λ_{max} .

5. Conclusions

The results obtained show conclusively that the incorporation of films of insulating polyaniline (emeraldine base, EB) between the emissive polymer, PPV-PPyV, and the electrode materials, ITO and Al, Cu or Au, drastically change the properties of the devices. The polyaniline greatly enhances the net ease of transfer of both electrons and holes between the electrode materials and the PPV-PPyV, consistent with the presence of an energy injection barrier between the PPV-PPyV and the electrode that is greatly reduced by the polyaniline which interacts beneficially with the electrode materials and/or the PPV-PPyV. In the absence of polyaniline the energy barriers mask the true effect of the work functions of the electrode materials on the injection of holes or electrons into the PPV-PPyV. The reduction in the energy injection barriers, due to the presence of polyaniline, permits the properties of the devices to be controlled more directly by the work functions of the electrode materials.

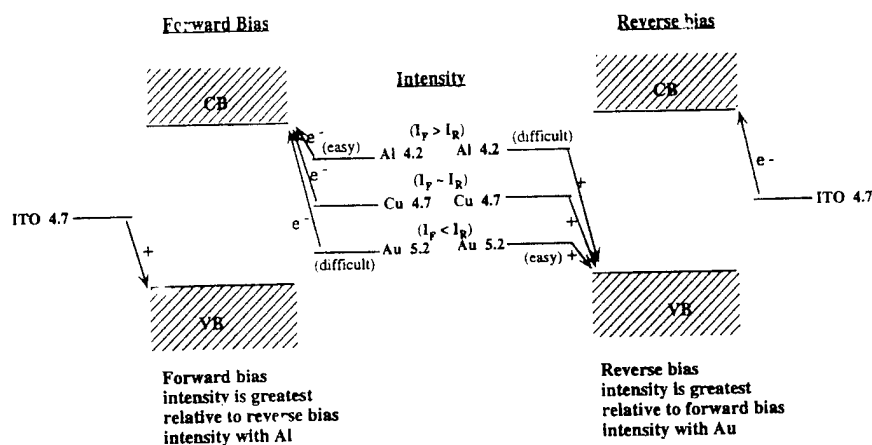


Fig. 10. Schematic representation of electron- and hole-injection processes in forward and reverse bias modes using Al, Cu and Au electrodes with ITO as a common electrode in each case. Corresponding work functions are given beside each electrode. I_F is intensity of emitted light in forward bias mode; I_R is intensity of emitted light in reverse bias mode.

The relative energies of the band edges [26] of the emissive polymer, PPV-PPyV, and the work function of the electrode materials are depicted schematically in Fig. 10. They are in qualitative agreement with the experimental results presented in this study when comparing forward and reverse bias behavior in a given device utilizing a given metal. It is assumed that, in forward and reverse bias modes in each device, the intensity of light emitted will be controlled by the minority carriers; conversely, the current density will be controlled by the majority carriers.

In the case of Al, in the forward bias mode, the injection of holes (minority carriers) from ITO into the valence band requires less energy than the injection of holes (minority carriers) from Al into the valence band in the reverse bias mode. This is consistent with the experimental intensity of emitted light being greater in the forward bias mode than in the reverse bias mode. Analogously, the experimental current density (electrons, majority carriers) is greater in the forward bias mode; it is easier for electrons to be injected from the Al to the conduction band (forward bias mode) than from the ITO to the conduction band (reverse bias mode).

In the case of Au, the reverse phenomena are observed; i.e., in the forward bias mode, the injection of electrons (minority carriers) from Au into the conduction band requires more energy than the injection of electrons (minority carriers) from ITO into the conduction band in the reverse bias mode. This is consistent with the experimental intensity of emitted light being greater in the reverse bias mode than in the forward bias mode. Analogously, the experimental current density (holes, majority carriers) is greater in the reverse bias mode; it is easier for holes to be injected from the Au to the valence band (reverse bias mode) than from the ITO to the valence band (forward bias mode).

In the case of Cu, the energy of injection of electrons into the conduction band and of holes into the valence band is taken to be approximately the same in both forward and reverse bias modes. This is consistent with the similarity of both the intensity of the emitted light and of the current density in both forward and reverse bias modes.

It should be noted that the qualitative model given in Fig. 10 cannot, of course, be used for comparing relative intensities of emitted light or current densities between devices utilizing different metals because of the experimental difficulties in exactly reproducing thicknesses of three different polymer layers in three different types of devices. Moreover, as mentioned above, we expect the polyaniline to interact in a chemically different manner with Al, Cu and Au, resulting in different reductions of electron and hole injection energies.

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